

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/DK05/000196

International filing date: 22 March 2005 (22.03.2005)

Document type: Certified copy of priority document

Document details: Country/Office: DK
Number: PA 2004 00469
Filing date: 23 March 2004 (23.03.2004)

Date of receipt at the International Bureau: 11 April 2005 (11.04.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse



Kongeriget Danmark

Patent application No.: PA 2004 00469

Date of filing: 23 March 2004

Applicant:
(Name and address) Technical University of Denmark
Building 101A
Anker Engelundsvej 1
DK-2800 Kgs. Lyngby
Denmark

Title: Ammonia storage

IPC: H 01 M 8/06

This is to certify that the attached documents are exact copies of the above mentioned patent application as originally filed.



Patent- og Varemærkestyrelsen
Økonomi- og Erhvervsministeriet

23 March 2005

Susanne Morsing
Susanne Morsing

23 MRS. 2004

Modtaget

AMMONIA STORAGE

TECHNICAL FIELD

This invention relates to the use of an ammonia storage device containing a metal ammine complex for reversible storage of ammonia in solid form. Upon release, ammonia is used either directly as a fuel in fuel cells or decomposed into dihydrogen and dinitrogen, which after an optional purification step can be used as a fuel in fuel cells.

BACKGROUND OF THE INVENTION

The potential advantages of using fuel cells have received significant attention. Application of dihydrogen or ammonia as a fuel, e.g., in fuel cells is attractive because it generates no polluting emissions [Hoogers, Thompsett, CatTech 2000, 3, 106]. In large-scale production facilities, dihydrogen or ammonia is produced from coal, naphta or natural gas [Dybkjær, in Ammonia: Catalysis and Manufacture (Ed. Nielsen), Springer, 1995] and steam and air. This obviously generates CO₂ but by application of appropriate sequestration strategies [Lackner, Annu. Rev. Energy Environ. 2002, 27, 193], ammonia or dihydrogen can, if desired, be produced without any net release of carbon oxides. So far, the main focus has been on using dihydrogen as a fuel. However, this attractive application has been hindered due to problems of storing sufficient amounts of dihydrogen in gaseous and even in liquid forms [Schlapbach & Züttel, Nature 2001, 414, 353]. To overcome this difficulty, various solid hydrogen storage materials have been proposed but the gravimetric hydrogen storage capacity is still low and the reversible storage and release of hydrogen requires relatively high pressure and temperature. Currently, attention is focused at the use of complex chemical hydrides [WO 03/04553 A2] but there are still no materials that fulfil the specifications defined by The US Department of Energy [www.energy.gov]. Since dihydrogen cannot yet be stored with a sufficient volumetric efficiency, alternatives have been investigated. Among the most promising sources of dihydrogen, methanol has attracted significant attention both as a possible source of dihydrogen that can be easily transported or for use in the direct methanol fuel cell [Hogart, Prospects of the direct methanol fuel cell, Fuel cell technology handbook (2003)]. However, compared to dihydrogen or ammonia as a fuel this

would require both central CO₂ sequestration at the methanol production facility and also decentral sequestration at each operating fuel cell, if all harmful contributions to the ecobalance should be avoided. Similar problems are necessarily encountered with all other carbon-containing fuels for fuel cells, such as e.g., methane, gasoline, diesel and ethanol. Ammonia is already produced in large facilities with daily production capacities that can be in excess of 3000 metric tons. It has been calculated that in terms of overall efficiency, ammonia is an attractive alternative to methanol [Metkemeijer & Achard, *Int. J. Hydrogen Energy* 1994, 19, 535].

Ammonia or ammine complexes, i.e. coordination compounds in which ammonia is bound to a metal ion have been known since the 19th century and many such compounds are today considered classical inorganic compounds. In the early literature, ammine complexes were often formed by reaction of metal salts with gaseous ammonia. Similarly, in many cases it was shown that new compounds containing less or even no ammonia could be formed by controlled thermal degradation of various ammine complexes. It has been suggested that such metal-ammine complexes might be used to increase the efficiency of ammonia production plants by allowing easy separation of ammonia from the equilibrium mixture by pressure swing adsorption [Liu & Aika, *Chem. Lett.* 2002, 798].

It is well-known in the art that ammonia can be used directly as a fuel for certain high-temperature fuel cells [Wojcik, Middleton, Damopoulos, van Herle, *J. Power Sources*, 2003, 118, 342]. Similarly, it is known that ammonia can be decomposed catalytically to mixtures of dihydrogen, dinitrogen and unreacted ammonia, which can be used directly as a fuel in e.g., alkaline fuel cells (AFC) [Kordesch et al., *J. Power Sources* 2000, 86, 162], but only after removal of ammonia traces in other types, such as in proton exchange membrane (PEM) fuel cells [Chellappa et al., *Appl. Catal. A.*, 2002, 227, 231]. Currently, an infrastructure that allows transportation of liquid ammonia, primarily for use in agriculture, already exists. Furthermore, ammonia is one of the chemicals of which the largest amount is produced on a worldwide basis. Thus, there are many possible advantages of using ammonia for reversible hydrogen storage. However, one particular disadvantage has prohibited the possibility for developing this technology, and this is the difficulty of convenient and safe transportation of ammonia [Schlög, *Angew. Chem. Int. Ed.* 2003, 42, 2004]. The use of ammonia stored as liquid in pressurized containers at room temperature may result in uncontrolled release of large quantities of toxic ammonia in case of physical damage

on a container. It is an object of the present invention to overcome this difficulty and to make efficient use of ammonia as a fuel in fuel cells and/or as a source of pure dihydrogen also for use in fuel cells.

DISCLOSURE OF THE INVENTION

The present invention relates to the use of an ammonia storage device holding a metal-ammine salts as solid storage media for ammonia, which in turn is used, either in its pure form or after decomposition to a gas mixture containing dinitrogen and dihydrogen, as a feedstock for an energy producing unit such as a fuel cell. The metal-ammine salt is a salt that releases ammonia upon heating, where it constitutes an ammonia releasing salt. After all, or part of the contained ammonia is released from the metal-ammine, it is possible to adsorb ammonia to the resulting solid, and the salt constitutes an ammonia absorbing salt. Thus, the metal-ammine salt constitutes a solid storage medium for ammonia, which represent a safe and practical option for storage and transportation of ammonia. Ammonia is released from the preferred metal ammine salt by heating the salt to temperatures in the range of 10-400 °C. Useful metal-ammine salts have the general formula $M(NH_3)_nX_z$, where M^{z+} is one or more metal ions capable of binding ammonia (preferred choices are $M = Li, Mg, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn$), n is the coordination number (2-8), and X is one or more anions, where preferred examples are $X = F, Cl, Br, I, SO_4, MoO_4, PO_4$ etc. The heat required to release the ammonia is generated by electrical resistive heating and/or from an exothermic chemical reaction and/or by heat exchange with the energy producing unit. In cases where ammonia is decomposed into dihydrogen and dinitrogen, the required heat is similarly generated by electrical resistive heating and/or from an exothermic reaction and/or by heat exchange with the energy producing unit. The present invention can be useful for large energy producing facilities, but by use of small rechargeable and/or replaceable ammonia storage containers combined with micro-fabricated/miniaturized ammonia decomposition reactors, it is also possible to provide energy for mobile units and portable devices. The preferred method of heating depends on which type of fuel cell is used, and particularly on the operating temperature of the fuel cell. However, in all cases there is a significant advantage of supplying the heat necessary for ammonia desorption and for the possible ammonia decomposition directly from the fuel cell through electrical

resistive heating or indirectly through heat exchange either with the fuel cell itself or from heat generated by controlled combustion of the exit gas from the fuel cell. The heat can also be generated by directly using a minor fraction of the dihydrogen from the decomposition unit in a combustion reaction.

During release of ammonia the original metal-ammine salt $M(NH_3)_nX_z$ is gradually transformed into $M(NH_3)_mX_z$ with $m < n$. When all the desired ammonia has been released, the resulting $M(NH_3)_mX_z$ is converted back into $M(NH_3)_nX_z$ by an absorption treatment with an ammonia-containing gas stream. Preferably, the adsorption of ammonia is done at a temperature below 100 C simply by passing the ammonia containing gas through the ammonia absorbing salt.

Typical hydrogen contents of the metal ammine complexes are in the range of 3-14wt%, preferably above 5 wt%. For several metal-ammine salts it is possible to release all ammonia and then transform the resulting material back into the original metal-ammine salt in a large number of cycles. This obviously constitutes preferred embodiments. For mobile units and for small portable devices, it is particularly useful to hold the metal-ammine in a container that can be separated from the fuel cell and recharged with ammonia in a separate recharging unit.

Supplying power to microelectronic or microelectromechanical systems suffers from the paradox that the power-generating unit is often larger than the device itself and for remote and autonomous operation the energy density has to be increased dramatically as compared to even the best lithium-ion battery technology [Holladay, Jones, Phelps and Hu, J.Power Sources 108 (2002) 21-27]. To increase the energy density micro sized fuel cells are developed, but again the main problem is the hydrogen storage. Using hydrocarbons as for example methanol needs many steps of evaporating, reforming and CO cleanup together with both liquid and gas handling that are difficult to integrate and control on a chip. The ammonia storage device combined with an ammonia tolerating fuel cell greatly simplifies the integration and control on a chip and increases the energy density by an order of magnitude compared to battery technology.

The invention is further described in the drawing, which illustrates the main components of the invention.

DESCRIPTION OF THE DRAWING

The ammonia storage container of the ammonia storage device (a) holds the solid metal-ammine salt, which releases ammonia gas upon heating. The ammonia storage container is operated at temperatures between 10 and 400 °C. The ammonia gas flows from the storage container into an optional catalytic ammonia decomposition unit (b) that converts ammonia into a stream containing mainly dihydrogen and dinitrogen. The flow of ammonia through the process unit will automatically be generated by the slight increase in pressure in the storage unit due to the increase in ammonia pressure above the heated metal-ammine during the release. The catalytic ammonia decomposition reactor contains one or more catalysts active for decomposition of ammonia and is operated at temperatures between 250 and 600° C. From this unit the gas enters an optional purification unit (c), which removes most unreacted ammonia either by adsorption at temperature below 200 C or by further ammonia decomposition at a temperature higher than that of the main catalytic ammonia decomposition unit (b). The fuel cell (d) is operated on (1) ammonia coming directly from the ammonia storage unit (a) or (2) a dihydrogen/dinitrogen mixture coming directly from the ammonia decomposed (b) or (3) a purified dinitrogen/dihydrogen mixture coming from the purification unit (c). The heat required to release the ammonia from the ammonia storage unit and, if needed, to decompose ammonia in the catalytic unit, is generated either through resistive heating using current from the fuel cell, or by controlled combustion of one of the optional streams going to the combustion unit, or by heat exchange directly with the fuel cell unit/product gas.

What is claimed is:

1. An ammonia storage device comprising:

- (a) a container;
- (b) an ammonia absorbing and releasing salt contained in said container;
- (c) means for heating said container and said ammonia absorbing salt for releasing ammonia in gas phase.

2. The ammonia storage device according to claim 1 further comprising means for adding ammonia to saturate the ammonia absorbing and releasing salt with ammonia.

3. The ammonia storage device according to claim 1, wherein said ammonia absorbing and releasing salt is an ionic salt of the general formula containing: MX_n .
4. The ammonia storage device according to claims 1-3, where said ionic salt is deposited as a fine powder of microcrystals or on a porous support material.
5. The ammonia storage device according to claim 1-3, where said means for heating is provided by electrical resistive heating.
6. The ammonia storage device according to claim 1-3, where said means for heating is provided by a heat produced by chemical reactions.
7. The ammonia storage device according to claim 1 where said container and means for heating are microfabricated using processes such as mechanical grinding, chemical vapour deposition (CVP), plasma enhanced chemical vapour deposition (PECVD), electron cyclotron resonance (ECR), sputtering, etching, lithographic methods such as electron beam lithography, photo lithography, or laser lithography.
8. A power generating unit comprising:
 - (a) an ammonia storage device according to claim 1;
 - (b) a fuel cell for converting ammonia directly into electric power; and
 - (c) connections between part (a) and (b).
9. A power generating unit comprising:
 - (a) an ammonia storage device according to claim 1;
 - (b) a reactor for dissociating ammonia into hydrogen and nitrogen;
 - (c) a fuel cell for converting hydrogen into electric power; and
 - (d) connections between the parts (a), (b), and (c).
10. The power generating unit according to claim 9 where said reactor for dissociating ammonia contains a heterogenous catalyst.
11. The power generating unit according to claims 9-10 where said heterogenous catalyst consists of a support and an active phase.

12. The power generating unit according to claims 9-11 where said active phase consists of dispersed nanoparticles of $\text{Co}_3\text{Mo}_3\text{N}$, Ru, Co, Ni and Fe or mixtures thereof.

13. The power generating unit according to claim 8 or 9, where excess hydrogen from said fuel cell provides heat through an oxidation reaction for heating said ammonia storage device.

14. The power generating unit according to claim 9 and 12, where excess hydrogen from said fuel cell provides heat through an oxidation reaction for heating said reactor for dissociating ammonia.

15. The power generating unit according to claim 8 or 9, where a fraction of the produced hydrogen bypasses the said fuel cell and provides heat through an oxidation reaction for heating said ammonia storage device.

16. The power generating unit according to claim 9 and 12, where a fraction of the produced hydrogen bypasses the said fuel cell and provides heat through an oxidation reaction for heating said reactor for dissociating ammonia.

17. The power generating unit according to claim 8 or 9, where ammonia provides heat through an oxidation reaction for heating said ammonia storage device.

18. The power generating unit according to claim 9 and 12, where ammonia provides heat through an oxidation reaction for heating said reactor for dissociating ammonia.

19. The power generating unit according to claims 9-18 where said connections are dimensioned to provide full balancing of the complete unit.

20. The power generating unit according to claim 8 or 9, used as miniature power source for microelectronic devices or micro-electro-mechanical-systems (MEMS).

21. The power generating unit according to claim 9 where said reactor for dissociating ammonia is microfabricated using processes such as mechanical grinding, chemical vapour deposition (CVP), plasma enhanced chemical vapour deposition (PECVD), electron cyclotron resonance (ECR), sputtering, etching, lithographic methods such as electron beam lithography, photo lithography, or laser lithography.

22. The power generating unit according to claim 9-10 where said reactor for dissociating ammonia is divided into two parts, one low temperature part that dissociates most ammonia and a high temperature part that dissociates the last present fraction of ammonia.

ABSTRACT

Solid metal-ammine complexes are applied for energy storage in connection with energy production in fuel cells. The compositional formula of the ammine complex is $M(NH_3)_yX_z$, where M^{z+} represents one or more metal ions capable of binding ammonia, X represents one or more anions, y is the coordination number (from 2 to 8), and z the valency of the metal ion (and thus the total number of compensating anion charges). Ammonia is released from the metal-ammine complexes by applying a temperature between 10-400°C. Ammonia is fed either directly to a fuel cell operated with ammonia as fuel, or to a catalytic reactor in which ammonia is decomposed mainly into dinitrogen and dihydrogen. The present invention can be useful for large energy producing facilities, but by use of small rechargeable and/or replaceable ammonia storage containers combined with micro-fabricated or miniaturized ammonia decomposition reactors, it is also possible to provide energy for mobile units and portable devices.

